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Letter

Visual valence bond rules for chemical reactions

Zexing Cao, Hui Xian, Wei Wu, Qianer Zhang

Department of Chemistry, State Key Laboratory for Physical Chemistry of the Solid Surface and Institute of Physical Chemistry,
Xiamen University, Xiamen 361005, China

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Abstract. A symmetry-adaptation rule of the valence bond structure for concerted reactions was developed within the bonded tableau valence bond formalism. According to a symmetry analysis of the valence bond structure segments accounting for the reaction, one can predict whether a chemical process is favored or unfavored. This method is based on conceptual resonance theory and the visual valence bond approach, without carrying out any explicitly theoretical calculations to know orbital details. Furthermore, by imposing a phase factor on each bonding pair, namely, the phase alternation postulate, the mechanisms of the concerted reactions can be easily outlined. These rules have been applied to organic and inorganic reactions including the participation of biradicals and species with multi-reference character.

Key words: Valence bond method – Symmetry rule – Phase alternation postulate – Chemical reaction

1 Introduction

The prediction of the course of a chemical reaction is an interesting subject for chemists. In the 1950s and 1960s, the frontier orbital approach of Fukui [1] and the conservation of orbital symmetry approach of Woodward and Hoffmann [2] were proposed based on a simple molecular orbital (MO) methodology: they are still useful tools for predicting organic concerted reactions. In the 1970s, using group theory approach and the localized bond idea, Pearson [3] expressed the conservation of orbital symmetry as “the bond symmetry rule”. The bond symmetry rule has been successfully used in inorganic reactions. From a generalized valence bond (GVB) point of view, the orbital-phase continuity principle (OPCP) was presented by Goddard [4]. The OPCP divides reactions into favored reactions (phase conditions satisfied), and unfavored reactions (phase conditions not satisfied). Symmetry plays no direct role in the OPCP. Based on generalized electron-pair wave functions and the primitive symmetry classification of the prinicpal structure of a molecular system, the VB approach to conservation of symmetry has been suggested [5]. The idea of permutational symmetry control was introduced to pericyclic reactions by van der Lugt and Oosterhoff [6, 7] and by Mulder and coworkers [8–10], and photoinduced electrocyclic reactions were discussed in terms of the VB orbitals of a cyclic system. The method is rather mathematical and complex. Subsequently, Kuwajima [11–13] used the spin- Hamiltonian methodology of VB theory to show $4n + 2$ and $4n$ rules appear in VB theory. Usually, the same predictions are made for these different rules. A few differences occur, but these result from ambiguity in the use of the method [3].

In recent years, the modern VB method has generated considerable interest because it preserves the close contact between the chemical picture and quantitative calculations [14–18]. In particular, the combination of modern VB theory in its spin-coupled form and intrinsic reaction coordinate calculations can interpret the chemical reaction mechanism very well [19, 20]. In VB theory, all electrons are coupled into bonding pairs and unpaired electrons, which from a VB structure. Generally, many coupling schemes, namely, many VB structures are responsible for a specific state. For a particular VB structure, there is usually no specific symmetry associated with the molecular point group, point group. Application of symmetry to the VB formalism is thus not as popular asin the MO method. Very recently, an approach to symmetrization of the bonded Young tableau bases has been used to construct the VB wavefunction for the low-lying states of molecules [21]. Introduction of symmetry to the VB structure permits the symmetry conservation principal to be expressed in a pictorial VB language. A symmetry adaptation of the VB structure is developed for the concerted reactions and is applied in a manner analogous to other symmetry procedures. Based on a picture of the localized bond in resonance theory (RT) [22, 23], a phase factor was im-

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Correspondence to: Zexing Cao

posed to mark the bonding pairs in a resonance structure. From the phase pattern of a resonance structure, the mechanisms for the concerted reactions can be schemed.

2 Symmetry of the VB structure

For a system with N electrons and spin S, the orbital part of the VB structure function ψ_k is defined as [24–27]

$$\psi_k = A_k e_{11}^{[\lambda]} \phi_0 = \left| \begin{array}{ll} 1 & 2 \\ \cdot & \cdot \\ 2p-1 & 2p \\ 2p+1 & \\ \cdot & \\ 2p+2S & \end{array} \right| , \tag{1}$$

where A_k is a normalization constant, $[\lambda] = [2^{N/2-S} 1^{2S}]$, $e_{11}^{[\lambda]}$ is a standard projection operator, $p = N/2 - S$, natural numbers $1, 2, \ldots,$ and $2p + 2S$ denote one-electron basis functions $\{\varphi_i\}$, and

$$\phi_0 = \varphi_1(1)\varphi_2(2)\ldots\varphi_N(N) \ . \tag{2}$$

Equation (1) is also referred to as a bonded tableau (BT) corresponding to the resonance structure with bonds 1–2, 3–4, ..., and unpaired electrons: $2p+1, \ldots, 2p+2S$.

Usually, single BT Eq. (1) corresponding to some VB structure is not of a specific symmetry associated with a molecular point group, so one has to use a projection operator associated with the molecular point group to symmetrize the BT bases [21]. The relationship between the symmetrized VB wavefunctions and the MO configurations for the ground and excited states of H_2 is shown in Table 1. The numbers 1 and 2 represent bonding atomic orbitals of hydrogen atoms.

If overlap-enhanced orbitals (OEOs) [28, 29] are employed, the ground state of H_2 can be described by one covalent structure $|1'2'|$ constructed from the optimized OEOs $1'$ and $2'$, and ionic VB structures can be ignored. This makes the wavefunction of the ground state become more compact. The correspondence shown in Table 1 can be considered as the VB form of a single σ bond in the ground and excited states, and a similar relationship exists for a single π bond. For the heteronuclear diatomic molecule LiH, the VB results show that a similar relationship exists among the dominant VB structures. These relationships display VB patterns for visually single chemical bonds in the ground and excited states.

3 The VB structure symmetry-adaptation rule

A chemical reaction is always related to bond-breaking and bond-making or valence electron rearrangement, and this valence electron behavior can be described by VB structure changes. According to RT, the evolution of a system in the elementary reaction process can be interpreted through resonances among the correlated VB structures including reactants, products and newly-created VB structures. Because only symmetry-adapted VB structures can effectively resonate, the change for the VB structure will thus retain symmetry consistent with the reactants in the elementary process. Therefore, we can postulate that the VB structures of the reactants and the products for the concerted reactions should preserve symmetry adaptation.

In fact, viewed from a VB structure picture, only partial VB structure segments are apparently involved in the reaction. The valence electrons forming these VB structure segments, as the electrons in the frontier orbitals of Fukui [1], would be most important and essentially dominate the reaction. Therefore, the VB structure symmetry adaptation should be based on these VB structure segments. Considering the possibility of energy partition and the geometrical conformation constraint, we can divide the resonance structure into certain sub-VB structures. For different sub-VB structures, the symmetry analysis for the VB structures can be carried out separately: namely, interactions between different sub-VB structures could be ignored. For example, we could postulate no resonance interaction between the σ electrons and the π electrons of the C=C double bond in the fixed nucleus approximation, and the four bonding electrons can be divided into two sub-VB structures responding to one σ bond and one π bond, respectively.

The detailed procedures of the symmetry analysis can be summarized as follows:

1. The VB structures of the reactants and products are drawn.
2. The valence electrons related to the reaction are picked out and the independent VB structure segments formed by these valence electrons are constructed.
3. Common symmetry between the reactants and products (or symmetry is maintained in the elementary process) is used to symmetrize the VB structure segments.
4. The symmetries of the symmetrized resultant VB structures of the reactants and the products are compared.

Table 1. Electronic molecular orbital (*MO*) configurations, valence bond (*VB*) wavefunctions and total energies (*E*) for the low-lying states of H_2[a]

State	MO	BT[b]	VB	E_{CI}	E_{VB}
$X^1\sum_g^+$	$\sigma_g^2\sigma_u^0$	$\vert 1\ 2\vert + (\vert 1\ 1\vert + \vert 2\ 2\vert)$	$H{-}H + (H{:}^- H^+ + H^+{:}\ H^-)$	−1.137284	−1.137284
$1^1\sum_u^+$	$\sigma_g^1\sigma_u^1$	$\vert 1\ 1\vert - \vert 2\ 2\vert$	$H{:}^- H^+ - H^+{:}H^-$	−0.168352	−0.168352
$2^1\sum_g^+$	$\sigma_g^0\sigma_u^2$	$\vert 1\ 2\vert - (\vert 1\ 1\vert + \vert 2\ 2\vert$	$H{-}H - (H{:}^-H^+ + H^+{:}H^-)$	0.483143	0.483143

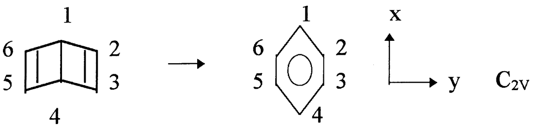
[a] H—H bond length is 0.74Å, energies in atomic units, basis set: STO-3G

[b] Coefficients of structures are omitted

When the VB structure symmetry adaptation is satisfied, we expect the concerted process to be favoered. The number of VB structures involved in the symmetry analysis is determined by linearly independent bonded Young tableau bass [30, 31] of relevant electrons. Within the OEO formalism, only covalent BTs are in demand for the ground-state molecules. We will refer to the use of the above rule as VB structure symmetry adaptation (VBSSA).

4 Application of the VBSSA rule

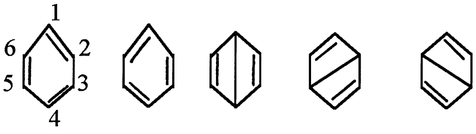
We now consider the isomerization of Dewar benzene into benzene



In reaction 3, the product benzene is of D_{6h} symmetry, but only the C_{2v} symmetry elements possessed in common with Dewar benzene are useful. We can therefore perform the symmetry analysis of the VB structures in the C_{2v} point group framework. There are six essential valence electrons involved in the reaction, numbered $1, 2, \ldots, 6$. These six valence electrons contribute to three localized bonds (two π bonds and one σ bond) in Dewar benzene, while the π bonds in benzene are delocalized, and these delocalized π bonds can be described by five independent BTs within the OEO formalism. Their corresponding BTs are

Dewar benzene |1 4|, |2 3|, |5 6|

Benzene



$$\begin{vmatrix}1&2\\3&4\\5&6\end{vmatrix}\quad\begin{vmatrix}1&6\\5&4\\3&2\end{vmatrix}\quad\begin{vmatrix}1&4\\5&6\\3&2\end{vmatrix}\quad\begin{vmatrix}1&6\\5&2\\4&3\end{vmatrix}\quad\begin{vmatrix}1&2\\6&3\\5&4\end{vmatrix}$$

Applying the projection operators associated with the C_{2v} point group on these BTs, we obtain

Dewar benzene

$$A_1: |1\ 4|,\quad |2\ 3| + |5\ 6| \qquad B_2: |2\ 3| - |5\ 6|$$

Benzene

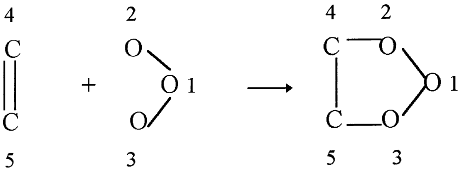
$$A_1: \begin{vmatrix}1&2\\3&4\\5&6\end{vmatrix} + \begin{vmatrix}1&6\\5&4\\3&2\end{vmatrix}, \quad \begin{vmatrix}1&4\\5&6\\3&2\end{vmatrix}, \quad \begin{vmatrix}1&6\\5&2\\4&3\end{vmatrix} + \begin{vmatrix}1&2\\6&3\\5&4\end{vmatrix};$$

$$B_2: \begin{vmatrix}1&2\\3&4\\5&6\end{vmatrix} - \begin{vmatrix}1&6\\5&4\\3&2\end{vmatrix}$$

$$A_2: \begin{vmatrix}1&6\\5&2\\4&3\end{vmatrix} - \begin{vmatrix}1&2\\6&3\\5&4\end{vmatrix}$$

Obviously, reaction 3 is forbidden by symmetry because no A_2 symmetrized VB structure segment in the reactant Dewar benzene can match the A_2 symmetrized VB structure segment of benzene.

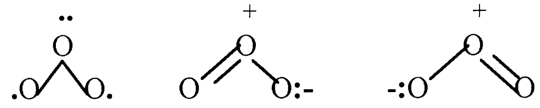
In the following, we consider the 1,3-dipolar addition of ozone with multireference character and olefin.



In reaction 4, the product of 1,3-dipole addition is only of the C_2 point group [32], whereas the reactants approach C_{2v} symmetry; however only the symmetry elements possessed in common with the product are useful. During reaction four π electrons from ozone and two π electrons from olefin are involved. These six electrons are arranged in five p orbitals, which are numbered $1, 2, \ldots, 5$. Their corresponding VB structures and BTs are

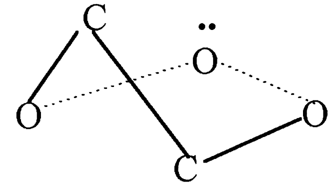
Olefin $C{=}C$ |4 5|

Ozone



$$\begin{vmatrix}1&1\\2&3\end{vmatrix}\qquad\begin{vmatrix}1&2\\3&3\end{vmatrix}\qquad\begin{vmatrix}1&3\\2&2\end{vmatrix}$$

Product



|2 4|, |3 5|, |1 1| .

Symmetrizing these BTs within the C_2 point group framework, we obtain

$$\text{Reactants}\quad A: |4\ 5|, \begin{vmatrix}1&1\\2&3\end{vmatrix}, \quad \begin{vmatrix}1&2\\3&3\end{vmatrix} + \begin{vmatrix}1&3\\2&2\end{vmatrix};$$

$$B: \begin{vmatrix}1&2\\3&3\end{vmatrix} - \begin{vmatrix}1&3\\2&2\end{vmatrix}.$$

$$\text{Product}\quad A: |1\ 1|, |2\ 4| + |3\ 5|;$$

$$B: |2\ 4| - |3\ 5| \ .$$

Therefore, the concerted process of 1,3-dipolar addition for reaction 4 is favored.

Figure 1 shows the changes in the VB structure symmetry for several representative reactions of the ground state molecules, where the numbers $1, 2, \ldots,$ indicate the bonding atomic orbitals. According to the VBSSA rule, for the reactions in Fig. 1, only the 1,4-addition for H_2 and butadiene and the electrocyclization

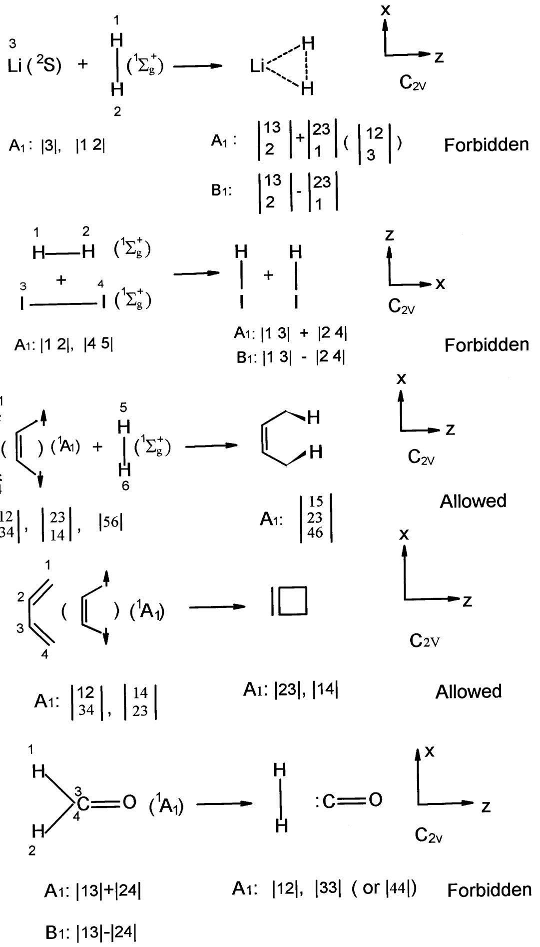


Fig. 1. The valence bond (*VB*) structure symmetry for the ground-state reactions

of butadiene are symmetry allowed, namely, favored, while dimolecular reaction of H_2 and I_2 with a four-center transition state in C_{2v} symmetry, the molecular decomposition of formaldehyde following the A_1 normal mode, and the broadside attack reaction of Li and H_2 all are unfavored. In the product butene, the newly created C—H bonds 1-5 and 4-6 are correlated with the π bond 2-3 by superconjugation interactions, and bonds 2-3, 1-5 and 4-6 should be classified as the same sub-VB structure and considered together.

From Fig. 2, we can see that the reactions in which one of reactants is in the suitable excited state are symmetry allowed. For example, in the addition reaction of singlet $O_2(^1\Delta_g)$ with ethene, the π electrons of singlet $O_2(^1\Delta_g)$ have multireference character. Two Slater determinants are needed to describe the electron configuration, namely, $KK\sigma_g^2\sigma_u^2\sigma_g^2(\pi_x^2 - \pi_y^2)$. According to the correspondence between MO theory and RT in the description of the electronic structure [33], this π-electron character can be expressed as $|1\ 2| - |3\ 4|$ in the BT formalism, where the numbers 1, 2, 3 and 4 indicate four p atomic orbitals of two oxygen atoms. When singlet $O_2(^1\Delta_g)$ approaches ethene in a twisted C_2 symmetry, the elementary process can be expected to be favored according to the VBSSA rule.

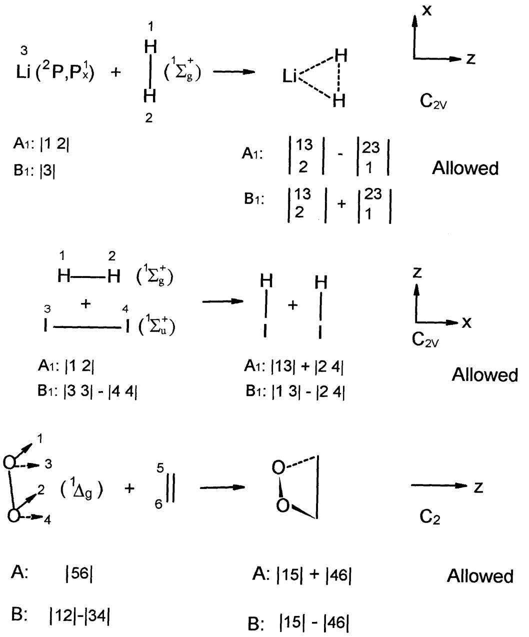


Fig. 2. The VB structure symmetry for reactions of the ground and excited states

5 Phase postulate

In RT a resonance structure is composed of certain components including two-centered bonds, lone pairs or unpaired electrons. The phases of these components of the resonance structure are not explicitly considered, and the total energy is independent of the phases between the components. However, from a simple symmetry-adaptation point of view, the atomic orbitals with the same phase may overlap to make a bond if the geometrical symmetry is allowed. Thus, if arbitrary phase are assigned to these components, the localized bond pattern will become confused when the phases of atomic orbitals are displayed explicitly. Some possible phase patterns of atomic orbitals contributing π bonds and lone electrons in butadiene and in the propene radical are shown in Fig. 3. For butadiene the phase patterns b and d should be assigned to the resonance structures I and II, respectively, in order to clarify the localized bonds, even though a pattern may not lead to change in energy. Similarly, patterns f and h will account for the resonance structures III and IV of the propene radical, respectively. Therefore, we can postulate that the phase among the localized bonds or between the localized bond and lone electron orbital in the resonance structure should be different each other so as to maintain a clear localized bond picture, namely, phase alternation. Certainly, this phase alternation hypothesis is meaningful only for the components interacting on each other through conjugation and superconjugation. The resonance between the correlated resonance structures exchanges the bonding patterns, and a phase change will take place, as shown in Fig. 3. For simplicity we will denote such a case as a "resonance phase change (RPC)." Assignment of the bond phase exposes a clear pattern of the bonding atomic orbitals, and according to this pattern one can

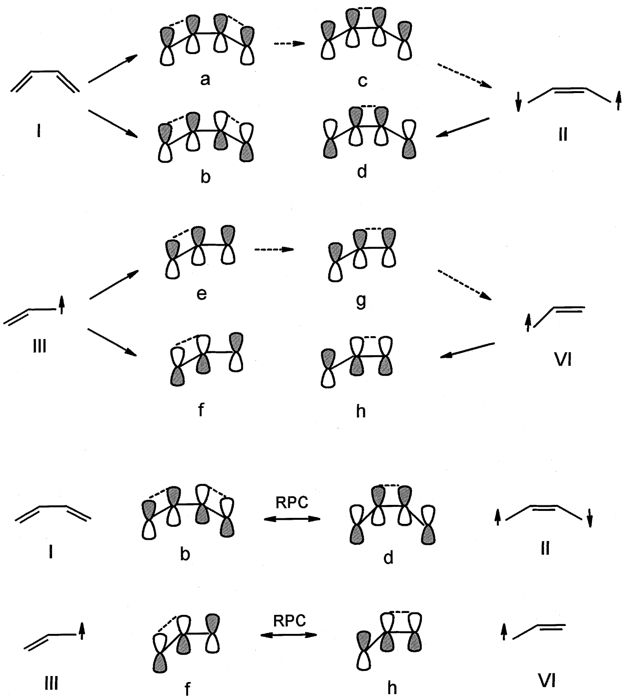


Fig. 3. Phase patterns of the localized bonds and resonance phase change (*RPC*)

predict the favored mechanism. It must be mentioned that the previous VBSSA rule is irrelevant with respect to the phase postulate.

In fact, the phase factor of a time-dependent orbital will change periodically with time. Assignment of the phase factor for a single atomic orbital is thus nonsignificant. However, when the orbitals contribute to bonding and form some resonance structure, their phases should change concordantly so as to keep a large overlap between the bonding orbitals and a smaller net mixing among the bonding pairs. The phase alternation among the interactive bonding pairs should be satisfied within the RT formalism for some resonance structure.

6 Application of the phase rule

6.1 Electrocyclic reactions

Consider now the electrocyclic reactions, such as cyclobutene ↔ *cis*-1,3-butadiene, as indicated in Fig. 4.

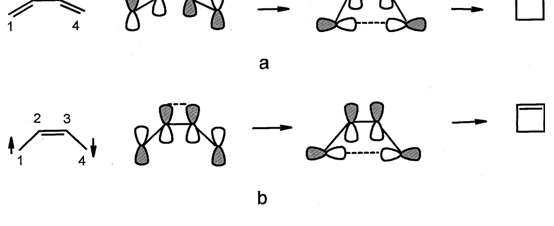


Fig. 4. Electrocyclizations of butadiene in **a** the ground state and **b** the excited state

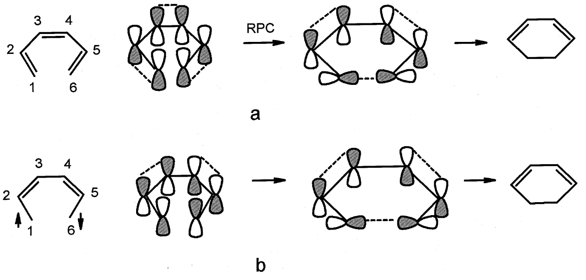


Fig. 5. Electrocyclizations of 1,3,5-hexatriene in **a** the ground state and **b** the excited state

From the phase pattern it can be seen that making bond 1-4 requires that the rotations at 1 and 4 be in the same direction, and hence the conrotatory mode is favored. Along with 1-4 bond making, a RPC between atoms 2 and 3 takes place and forms bond 2-3. For the excited state of butadiene, the butene diradical resonance structure is responsible for the excited state. Figure 4 also shows the phase pattern of the resonance structure of the first singlet excited state, and it is obvious that to make bond 1-4 the rotations at 1 and 4 must be in opposite directions: that is, only the disrotatory mode is favored.

Similarly for the electrocyclization of 1,3,5-hexatriene, we see in Fig. 5 that the electrocyclization of the ground state would be in a disrotatory mode, while the electrocyclization of the first singlet excited state is a conrotatory mode.

6.2 Sigmatropic reactions

We consider the hydrogen migration in a system such as 1,3-pentadiene, as illustrated in Fig. 6. Here the C—H bond involved in the reaction is correlated with π bonds by superconjugation interactions, and the phase for C—H should differ from the nearest π bond according to the phase alternation postulate. We see that [1, 5] migration is allowed and that the H would be expected to stay on the same side of the plane (suprafacial) during the reaction. Similarly, the [1, 3] and [1, 7] migrations are pictured in Figs. 7 and 8; however, the H must pass through the plane of the molecule (antarafacial), as expected. A phase pattern for the [3, 3] sigmatropic reaction in which the 1-1′ bond is correlated with two π bonds by superconjugation interactions is shown in Fig. 9. From this phase pattern, the shift of the

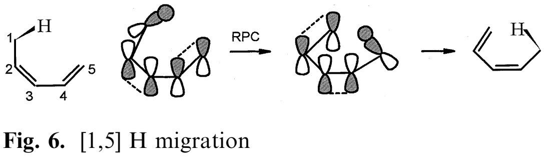


Fig. 6. [1,5] H migration

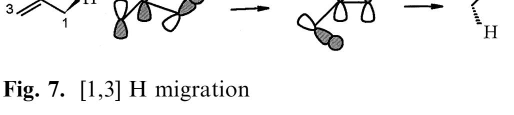


Fig. 7. [1,3] H migration

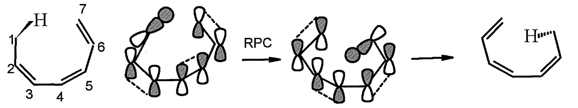


Fig. 8. [1,7] H migration

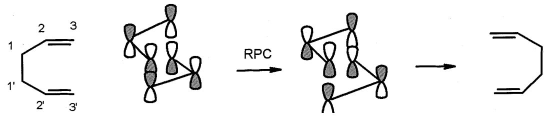


Fig. 9. [3,3] σ-bond migration

σ bond from 1-1′ to 3-3′ should be a favored concerted process.

7 Comparison of the VBSSA and the phase postulate methods with previous approaches

It is well known that the Hofmann–Woodward approach and the OPCP are based upon the MO (Hartree–Fock method) and the GVB orbital (the GVB method), respectively, and the frontier orbital method analyzes the highest occupied molecular orbital and the lowest unoccupied molecular orbitals, whereas the present VBSSA rule and the phase postulate are based on a traditionally visual VB structure pattern. The fundamental foundations of these methods are thus different. The MO method within the single-reference formalism does not properly describe bond-breaking and bond-making and might perform very poorly for the description of the reaction which involves intermediates with multireference character. Resonances among several correlated VB structures can account for the multireference character, thus, the VBSSA approach should be more widely applicable.

Like other rules, the VBSSA rule only concerns partial valence electrons involved in reactions instead of all electrons. If these partial valence electrons can be considered as two-centered bonding pairs without conjugation and superconjugation interactions among them, the VBSSA rule falls in line with the bond symmetry rule of Pearson [3]. Unlike the earlier VB approaches [5–10], the VBSSA divides the VB structure into certain sub-VB structures according to conjugation and superconjugation interactions, and compares symmetries of possible resultant sub-VB structures between the reactants and products.

In the OPCP rule, every electron is in a different orbital and each orbital can be delocalized over several atoms. The GVB calculation on some simple atom-exchange reactions [4] established that the phase of the nonbonding orbital changes sign in order to minimize overlap with each of the orbitals of a bonding pair. If the general nature of the GVB orbitals during reaction can be transferred to other molecules, it becomes relatively easy to predict chemical reactions. In the present phase postulate, the phases are only marks to clarify the VB picture visually, for all components correlated by conjugation and superconjugation interactions, such as two-centered bonds, lone pairs and unpaired electrons in a VB structure. From a phase pattern one can easily predict the favored mechanism of a reaction. Only conceptual knowledge of the VB approach or the resonance theory is needful for use of the VBSSA and the phase postulate methods, without carrying out actually theoretical calculation.

8 Conclusions

Conservation of symmetry can be expressed as "the symmetry adaptation of the VB structure" in visual VB language, which can predict chemical reactions by performing symmetry analysis of related VB structure segments accounting for the reaction. Unlike other methods, the VBSSA approach is based on the bonding pattern in the resonance structure, and does not need the MOs or GVB orbitals obtained from theoretical calculations for the reactants and products. In fact, the VB approach is another valid formalism describing the electronic structure, much as MO theory, therefore, the justification of the VB structure symmetry rule analogous to the MO or GVB orbital approaches might be taken for granted. Introduction of the phase postulate allows the mechanism for intramolecular concerted reactions to be predicted in a simple and visual manner. Applications of the VBSSA and the phase postulate to a number of reactions show that they are very useful tools, even though they are derived from a pictorial VB formalism.

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